



IR and UV study of reversible water-induced structural transformations of poly(manganese 1,1'-ferrocenediyl-bis(*H*-phosphinate)) and poly(cobalt 1,1'-ferrocenediyl-bis(*H*-phosphinate))

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ARTICLE INFO

Article history:

Received 30 December 2017

Received in revised form

6 April 2018

Accepted 9 April 2018

Available online 12 April 2018

Keywords:

Metal-organic frameworks

Ferrocenylphosphinic acids

UV–Vis and vibrational spectroscopy

Crystal-to-amorphous transformation

ABSTRACT

Recently new flexible and hydrolytically stable metal-organic framework $[M(H_2O)_2(FC(PhOO)_2) \cdot 2H_2O]_n$, $M = Co$ has been synthesized by the use of synthetic technique, described earlier for $M = Mn$ [1]. The heating of both complexes leads to elimination of water molecules and in the case of Co complex is accompanied by change of its color from orange to dark blue. The corresponding structural changes are reversible and are reflected in vibrational and electronic absorption spectra. Analysis of IR, Raman and UV–vis spectra of complexes shows the same structures of Mn and Co complexes before and after heating and suggests that both Mn and Co coordination polyhedra undergo reversible changes under heating from octahedral to tetrahedral form with ferrocene part remaining unchanged.

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1. Introduction

Metal-organic frameworks (MOFs) or porous coordination polymers (CPs) attract wide attention [2–7] due to their large structural diversity allowing for numerous potential applications: gas storage, catalysis, ion exchange, molecular magnetism, luminescence, sensing, medicine, etc. [8–15] Flexible or dynamic MOFs can undergo reversible structural transformations upon adsorption/desorption of guest molecules [16]. The fascinating flexibility phenomena in MOFs offer a wide range of application opportunities emerging when structural transformations upon adsorption/desorption are accompanied by the simultaneous changes of physical properties: the color of the MOFs, adsorption selectivity, proton conductivity, luminescence and magnetic properties [17–23]. The transformations may be accompanied by the cleavage and formation of coordination bonds, by the change of the

framework dimensionality, by the change of the metal coordination polyhedra, the slippage of the layers, mechanical shrinkage of crystals, etc [24–29]. In these processes the crystallinity is often retained, but in some cases the crystalline – to – amorphous – to crystalline transformations take place [5,16,24,28]. Typically flexible porous coordination polymers are formed by metal ions linked by organic ligands such as carboxylates or N-donating linkers. Using of P-containing ligands as phosphinate or phosphonate fragments is not so popular due to their conformational lability. At the same time in combination with such 3D rigid fragment as ferrocene (Fc) they may be used for formation of porous coordination polymers with wide structural diversity. Fc represents popular backbone for a variety of chelate ligands because the presence of a Fc unit provides i) a convenient 3D environment for building various chelating structures, ii) the possibility of planar chirality (in addition to atom chirality in the side branches), and iii) a well-defined electrochemical response sensitive to the changes in the ligating branches (conformation, coordination, donor–acceptor and Lewis acid–base interactions). Ferrocenylphosphinous acid existing as a mixture of two tautomeric forms has been widely employed as

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